PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2002-179762
(43)Date of publication of application : 26.06.2002

(51)Int.Cl. C08G 59/14
C08G 59/20
C09D161/06
C09D163/02
C09D183/10
C09J161/06
C09J163/02
C09J183/10

(21)Application number : 2000-374676
(22)Date of filing : 08.12.2000

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(54) SILANE-MODIFIED EPOXY RESIN COMPOSITION AND CURED PRODUCT THEREOF

(57)Abstract:
PROBLEM TO BE SOLVED: To obtain a silane-modified epoxy resin composition capable of producing a cured product having excellent heat resistance and causing no void or crack, and to obtain a cured product from the composition.
SOLUTION: This silane-modified epoxy resin composition comprises an alkoxy group-containing silane-modified epoxy resin (A) obtained by de-alcoholic condensation reaction of an alkoxysilane partial condensation product (3) with a bisphenol-type epoxy resin mixture, and a curing agent (B) for epoxy resin, where the bisphenol-type epoxy resin mixture comprises a bisphenol-type epoxy resin (1) having an epoxy equivalent of >400 g/eq and <10,000 g/eq and a bisphenol-type epoxy resin (2) having an epoxy equivalent of >170 g/eq and <400 g/eq and the weight ratio of use ((1)/(2)) is 0.1 to 1.0. An epoxy resin-silica hybrid cured product is obtained by curing the epoxy resin composition.

LEGAL STATUS

[Date of request for examination]	08.12.2000
[Date of sending the examiner's decision of rejection]	
[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]	
[Date of final disposal for application]	
[Patent number]	3458379
[Date of registration]	08.08.2003
[Number of appeal against examiner's decision of rejection]	
[Date of requesting appeal against examiner's decision of rejection]	
[Date of extinction of right]	

CLAIMS

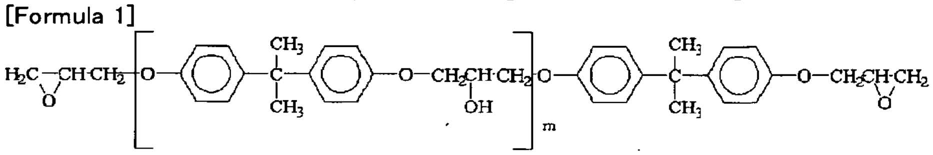
[Claim(s)]
[Claim 1] Weight-per-epoxy-equivalent 400 g/eq Exceed, exceed the bisphenol mold epoxy resin (1) of less than 10000 g/eq, and weight-per-epoxy-equivalent 170 g/eq, and the bisphenol mold epoxy resin mixture whose operating weight ratios ((1) /(2)) with the bisphenol mold epoxy resin (2) of under 400g / eq are 0.1-1.0 The silane modified epoxy resin constituent characterized by containing the alkoxy group content silane modified epoxy resin (A) which is made to carry out a dealcoholization condensation reaction to an alkoxysilane partial condensate (3), and is obtained, and the curing agent for epoxy resins (B).
[Claim 2] The silane modified epoxy resin constituent according to claim 1 with which a dealcoholization condensation reaction is performed to the bottom of a non-solvent.
[Claim 3] The silane modified epoxy resin constituent according to claim 1 or 2 whose weight (weight ratio) of the silica equivalent weight / bisphenol mold epoxy resin mixture of an alkoxysilane partial condensate (3) is 0.1-0.5.
[Claim 4] The silane modified epoxy resin constituent according to claim 1 to 3 whose alkoxysilane partial condensate (3) is a partial condensate of methyl trimetoxysilane.
[Claim 5] The epoxy resin constituent according to claim 1 to 4 which is at least one sort chosen from the group which the curing agent for epoxy resins (B) becomes from phenol novolak resin, cresol novolak resin, imidazole derivatives, a dicyandiamide, and a polyamide.
[Claim 6] The epoxy resin-silica hybrid hardened material characterized by coming to carry out the hardening reaction of the silane modified epoxy resin constituent according to claim 1 to 5.
[Claim 7] The epoxy resin-silica hybrid hardened material according to claim 6 which comes to carry out sol-gel hardening of the silane modified epoxy resin constituent at 40-150 degrees C.
[Claim 8] The epoxy resin-silica hybrid hardened material according to claim 6 which comes to carry out full hardening of the silane modified epoxy resin constituent at room temperature -250 degree C.
[Claim 9] The electrical and electric equipment and the insulating material for electronic ingredients which comes to contain at least one sort chosen from the group which consists of a silane modified epoxy resin constituent according to claim 1 to 5 and an epoxy resin-silica hybrid hardened material according to claim 6 to 8.
[Claim 10] The coating agent which comes to contain at least one sort chosen from the group which consists of a silane modified epoxy resin constituent according to claim 1 to 5 and an epoxy resin-silica hybrid hardened material according to claim 6 to 8.
[Claim 11] Adhesives which come to contain at least one sort chosen from the group which consists of a silane modified epoxy resin constituent according to claim 1 to 5 and an epoxy resin-silica hybrid hardened material according to claim 6 to 8.
[Claim 12] The coating agent according to claim 10 which is a coating.

[Translation done.]

DETAILED DESCRIPTION

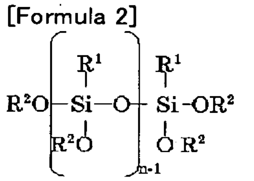
[Detailed Description of the Invention]
[0001]
[Field of the Invention] This invention relates to a silane modified epoxy resin constituent and its hardened material.
[0002]
[Description of the Prior Art] Conventionally, generally the epoxy resin is used as a constituent combined with the curing agent, and the object for prizes of this constituent has been carried out also in the electrical and electric equipment and electronic ingredient-related field. However, with development of the electrical and electric equipment and the electronic ingredient field in recent years, high performance is required more from the hardened material of an epoxy resin constituent, and heat-resistant improvement is desired especially.
[0003] In order to raise the thermal resistance of the hardened material of an epoxy resin constituent, in addition to the epoxy resin and the curing agent, the approach using the constituent which mixed fillers, such as a glass fiber, a glass particle, and a mica, is performed. However, thermal resistance sufficient by this approach is not obtained. Moreover, since the transparency of the hardened material obtained is lost and the adhesive property of the interface of a filler and an epoxy resin is moreover inferior, this approach of mechanical properties, such as a rate of expanding, is insufficient.
[0004] Moreover, the approach using the complex of an epoxy resin and a silica as an approach of raising the thermal resistance of the hardened material of an epoxy resin constituent is proposed (JP,8-100107,A). The complex concerned hydrolyzes and solates this alkoxysilane and is obtained by carrying out a polycondensation further and gelling while adding hydrolysis nature alkoxysilane to the solution of the partial hardened material of an epoxy resin and hardening this hardened material further. However, although thermal resistance improves to some extent as compared with an epoxy resin independent hardened material, the hardened material obtained from this complex originates in the water in complex, the water produced at the time of hardening, and alcohol, and a void (air bubbles) generates it in a hardened material. Moreover, if the amount of alkoxysilane is increased in order to raise thermal resistance further, in losing the transparency of the hardened material with which the silica generated by the sol-gel hardening reaction is obtained by condensing and milking, in order to solate a lot of alkoxysilane, a lot of water is needed, and the camber of a hardened material, a crack, etc. are caused as the result.
[0005] Moreover, the constituent (JP,3-201466,A) which combined the silane modified epoxy resin which made the silicone compound react to an epoxy resin, and the phenol novolak resin which is a curing agent, and the constituents (JP,61-272243,A, JP,61-272244,A, etc.) which combined the silane modified epoxy resin to which the bisphenol A mold epoxy resin, tetra-screw BUROMO bisphenol A, and a methoxy group content silicone intermediate product were made to react, and the phenol novolak resin which is a curing agent are also proposed. However, the main configuration unit of a silicone compound or a methoxy group content silicone intermediate product is a diorganopolysiloxane unit, and since the hardened material of these epoxy resin constituents cannot generate a silica, thermal resistance is all inadequate [the hardened material].
[0006]
[Problem(s) to be Solved by the Invention] This invention is excellent in thermal resistance, and aims at offering the silane modified epoxy resin constituent which can acquire the hardened material which moreover does not produce a void, a crack, etc., and the hardened material obtained from the constituent concerned.
[0007]
[Means for Solving the Problem] That this invention person should solve said technical problem, as a result of repeating examination wholeheartedly, it came to complete a header and this invention for the epoxy resin-silica hybrid hardened material corresponding to said purpose being obtained with the constituent which consists of an alkoxy group content silane modified epoxy resin which consists of a specific epoxy resin and a specific alkoxysilane partial condensate, and a curing agent for epoxy resins.
[0008] Namely, this invention Weight-per-epoxy-equivalent 400 g/eq Exceed, exceed the bisphenol mold epoxy resin (1) of less than 10000 g/eq, and weight-per-epoxy-equivalent 170 g/eq, and the bisphenol mold epoxy resin mixture whose operating weight ratios ((1) /(2)) with the bisphenol mold epoxy resin (2) of under 400g / eq are 0.1-1.0 It is related with the silane modified epoxy resin constituent characterized by containing the alkoxy group content silane modified epoxy resin (A) which is made to carry out a dealcoholization condensation reaction to an alkoxysilane partial condensate (3), and is obtained, and the curing agent for epoxy resins (B). Moreover, this invention relates to the epoxy resin-silica hybrid hardened material which makes it come to harden the epoxy resin constituent concerned.

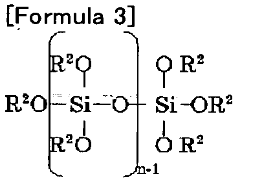
[0009]
[Embodiment of the Invention] As mentioned above, the bisphenol mold epoxy resin mixture which is the raw material of the alkoxy group content silane modified epoxy resin in this invention (A) exceeds weight-per-epoxy-equivalent 400 g/eq, exceeds the bisphenol mold epoxy resin (1) (only henceforth an epoxy resin (1)) of less than 10000 g/eq, and weight-per-epoxy-equivalent 170 g/eq, and consists of a bisphenol mold epoxy resin (2) of less than 400 g/eq, and (it only being hereafter called epoxy resin (2)). An epoxy resin (1) and an epoxy resin (2) are obtained by the reaction with halo epoxide, such as bisphenols, epichlorohydrin, or beta-methyl epichlorohydrin. What is obtained by oxidation by the peroxy acid of the thing; dihydroxy phenyl sulfide obtained as bisphenols by the reaction of aldehydes, such as a phenol or 2, a 6-dihalo phenol and formaldehyde, an acetaldehyde, an acetone, an acetophenone, a cyclohexanone, and a benzophenone, or ketones; what is obtained by the etherification reaction of hydroquinone etc. is raised.
[0010] An epoxy resin (1) and an epoxy resin (2) all have the hydroxyl group which can form a silicate by the dealcoholization condensation reaction with an alkoxysilane partial condensate (3). The hydroxyl group concerned needs to be contained in no molecules which constitute an epoxy resin (1) and an epoxy resin (2), and should just have the hydroxyl group as these resin.
[0011] Also in these bisphenols mold epoxy resin, the bisphenol A mold epoxy resin which used bisphenol A as bisphenols especially is most used widely, is a low price, and desirable.
[0012] The bisphenol A mold epoxy resin is general formula (a): [0013].
[Formula 1]



[0014] It is the compound come out of and expressed.
[0015] The epoxy resin (1) used by this invention exceeds weight-per-epoxy-equivalent 400 g/eq, is the thing of less than 10000 g/eq, and is 800 to about 20000 as number average molecular weight. When an epoxy resin (1) is the bisphenol A mold epoxy resin, the average of the repeat number of unit m in a general formula (a) is equivalent to 1.6-69. Since a flexible semi-hardening object (sol-gel hardened material) becomes the hydroxyl group in an alkoxysilane partial condensate (3) and the epoxy resin concerned which reacts decreases, and the content of the unreacted alkoxysilane partial condensate in the alkoxy group content silane modified epoxy resin which is obtained for the reason increases, and is hard to be obtained when the above-mentioned weight per epoxy equivalent is 400 or less g/eq, it is not desirable. On the other hand, when weight per epoxy equivalent is 10000 or more g/eq, an epoxy resin (1) and an alkoxysilane partial condensate (3) do not dissolve with reaction temperature, and a dealcoholization reaction cannot advance easily. In addition, as long as an epoxy resin (1) satisfies the above-mentioned range as weight per epoxy equivalent, even if the repeat number of unit m contains the thing of zero, it does not interfere.
[0016] Indispensable use of the epoxy resin (2) which is the raw material of the alkoxy group content silane modified epoxy resin in this invention (A) is carried out by the following reasons. That is, finally, full hardening (the condition that sol-gel hardening by the hydrolysis in an alkoxy group content silane modified epoxy resin (A) and condensation advanced in hardening by the ring breakage and crosslinking reaction of the epoxy group in an alkoxy group content silane modified epoxy resin (A) and an epoxy group with the curing agent for epoxy resins (B) and a list is said) of the silane modified epoxy resin constituent obtained is carried out, and it is used for the purpose application. However, for a specific application, it may be dealt with in the state of semi-hardening in the midcourse phase before carrying out full hardening, or may be produced commercially. In such a case, flexibility sufficient in the condition (the condition of having advanced only sol-gel hardening by the hydrolysis in an alkoxy group content silane modified epoxy resin (A) and condensation is said without carrying out ring breakage and crosslinking reaction of the epoxy group in an alkoxy group content silane modified epoxy resin (A) and an epoxy group with the curing agent for epoxy resins (B)) of semi-hardening is required. Therefore, this military requirement is satisfied to this invention by using together an epoxy resin (1) and an epoxy resin (2) at a predetermined rate as a configuration raw material of an alkoxy group content silane modified epoxy resin (A).
[0017] An epoxy resin (2) exceeds weight-per-epoxy-equivalent 170 g/eq, it is the thing of less than 400 g/eq, and number average molecular weight is 340 to about 800. When an epoxy resin (2) is the bisphenol A mold epoxy resin, the average of the repeat number of unit m in a general formula (a) is equivalent to 0-1.62. In addition, as long as an epoxy resin (2) satisfies the above-mentioned range as weight per epoxy equivalent, even if the repeat number of unit m contains one or more things, it does not interfere. Although mentioned later, when it is going to advance a dealcoholization condensation reaction under a non-solvent in order to use the alkoxy group content silane modified epoxy resin (A) obtained for a non-solvent application, the use meaning of an epoxy resin (2) is large. That is, it is because both may not fully dissolve with the reaction temperature concerned and an epoxy resin (2) will function as a compatibilizer in this case, if the dealcoholization condensation reaction of an epoxy resin (1) and the alkoxysilane partial condensate (3) is carried out to the bottom of a non-solvent. However, when weight per epoxy equivalent uses the bisphenol mold epoxy resin of 400 or more g/eq, this compatibility-ized effectiveness decreases, the inside of a system serves as an ununiformity at the time of a dealcoholization condensation reaction, and the reaction concerned stops being able to go on easily.

[0018] In this invention, it is made indispensable to use the bisphenol mold epoxy resin mixture which comes to use together an epoxy resin (1) and an epoxy resin (2) at a predetermined rate as mentioned above. It is because the purpose of this invention that it is flexible and the semi-hardening object (sol-gel hardened material) which is rich in workability can be easily prepared according to this concomitant use can be attained. Since the operating weight ratio of an epoxy resin (1) and an epoxy resin (2) influences greatly the engine performance of the epoxy resin constituent obtained or a semi-hardening object, the range of (1)/(2) must be 0.1-1.0, and it is preferably set to 0.2-0.8. Moreover, it is desirable to become 200 - 350 g/eq as the equivalent of the bisphenol mold epoxy resin mixture by which the epoxy resin (1) and the epoxy resin (2) were set. If the weight ratio concerned exceeds 1.0 or the equivalent of bisphenol mold epoxy resin mixture exceeds 350 g/eq, since the inclination gelled in the middle of an epoxy resin and a reaction becomes high, and the weight ratio concerned will be less than 0.1 or the amount of the alkoxysilane partial condensate (3) which remains in the alkoxy group content silane modified epoxy resin (A) which is a resultant when the weight per epoxy equivalent concerned is less than 200 g/eq will increase, neither is desirable.
[0019] Moreover, as an alkoxysilane partial condensate (3) which constitutes the alkoxy group content silane modified epoxy resin (A) in this invention, the following alkoxysilane compound and water can be added under existence of a **** base catalyst, and what was hydrolyzed and condensed partially can be used.
[0020] As the alkoxysilane compound concerned, it is (general formula b):R1pSi(OR2)4-p (p shows 0 or 1 among a formula.), for example. R1 shows the low-grade alkyl group which may have a functional group linking directly to a carbon atom, an aryl group, or partial saturation aliphatic series residue. R2 shows a methyl group or an ethyl group, and even if R2 comrades are the same respectively, they may differ. The compound expressed can be illustrated.
[0021] As the above-mentioned alkoxysilane which is the configuration raw material of an alkoxysilane partial condensate (3) being concrete, a tetramethoxy silane, a tetra-ethoxy silane, methyl trimetoxysilane, methyl triethoxysilane, ethyl trimethoxysilane, ethyltriethoxysilane, n-propyltrimethoxysilane, n-propyl triethoxysilane, isopropyl trimethoxy silane, isopropyl triethoxy silane, phenyl trimethoxysilane, phenyl triethoxysilane, etc. are raised.

[0022] Since what is obtained as the above-mentioned alkoxysilane partial condensate (3) from the methoxy silanes of the alkoxysilane compounds which are the configuration raw materials concerned is rich in reactivity with an epoxy resin (1) and an epoxy resin (2) and can prepare an epoxy resin-silica hybrid hardened material at low temperature comparatively, it is desirable. Moreover, among the alkoxysilane compounds which are the configuration raw materials concerned when the thermal resistance of a hybrid hardened material and thick-film-ization are taken into consideration, 3 organic-functions alkoxysilane (p= 1 in a general formula (b)) is desirable, and when especially versatility is taken into consideration, methyl trimetoxysilane is still more desirable.
[0023] An alkoxysilane partial condensate (3) is shown by the following general formula (c) or (d). General formula (c) : [0024]
[Formula 2]


[0025] (R1 shows among a formula the low-grade alkyl group which may have a functional group linking directly to a carbon atom, an aryl group, or partial saturation aliphatic series residue.) R2 shows a methyl group or an ethyl group, and even if R2 comrades are the same respectively, they may differ.
[0026] General formula (d) : [0027]
[Formula 3]


[0028] (Each of R1 and R2 is the same as them of a general formula (c) among a general formula (d).)
[0029] As for the average repeat number of unit n, in 230 to about 2000, a general formula (c), and (d), 2-11 are [the number average molecular weight of the alkoxysilane partial condensate (3) concerned] desirable. If the value of n exceeds 11, since there is an inclination for solubility to worsen, for compatibility with an epoxy resin (1) and an epoxy resin (2) to fall remarkably in reaction temperature, and for reactivity with an epoxy resin (1) to fall, it is not desirable. It will be distilled off by 1 [alcoholic] clue out of the system of reaction in the middle of a reaction that n is two or less, and it is not desirable.
[0030] An alkoxy group content silane modified epoxy resin (A) given in this invention is obtained by carrying out the dealcoholization condensation reaction of an epoxy resin (1), an epoxy resin (2), and the alkoxysilane partial condensate (3) to the bottom of existence of a solvent or a non-solvent. Although the weight of silica equivalent weight / bisphenol mold epoxy resin mixture of an operating weight ratio with an alkoxysilane partial condensate (3), i.e., an alkoxysilane partial condensate, (3), **, especially a limit are not set to the epoxy resin (1) and (2) concerned,

it is usually 0.1-0.5 and is 0.13-0.4 preferably. Here with the silica equivalent weight of an alkoxysilane partial condensate (3) It is weight when an alkoxy run partial condensate (3) becomes the silica which carries out a sol-gel hardening reaction and is expressed with (general formula e);R1pSiO (4-p) / 2 (each value in a formula is the same as a general formula (b)). Superfluous water is added to an alkoxysilane partial condensate (3), and it can compute by asking for the weight rate of the silica heated and generated at 120 degrees C. If there is little heat-resistant improvement and it exceeds 1.0 with the above-mentioned weight ratio being less than 0.1, a hybrid hardened material becomes weak and is not desirable.

[0031] As an epoxy resin (1), in addition, the thing of the 800 or more average weight per epoxy equivalent amount of macromolecules The case where it is used 0.7 or more by the weight ratio (epoxy resin (1) / epoxy resin (2)) of epoxy resin mixture, If it performs a dealcoholization condensation reaction until the hydroxyl group of an epoxy resin (1) and an epoxy resin (2) disappears completely in using the average repeat number of unit n> 7 of said general formula (c) as a use raw material as an alkoxysilane partial condensate (3), it will be easy to cause hyperviscosity-izing and gelation. In such a case, hyperviscosity-izing and gelation are prevented by the approach of stopping a dealcoholization reaction in the middle of a reaction. For example, when it has hyperviscosity-ized, the alcohol flowing out is flowed back, the amount of distilling off of the alcohol from the system of reaction can be adjusted, or the system of reaction is cooled and the approach of terminating a reaction can be adopted.

[0032] Manufacture of an alkoxy group content silane modified epoxy resin (A) can be performed under solvent existence or a non-solvent as mentioned above. In the dealcoholization condensation reaction in this invention, about 50-130 degrees C of reaction temperature are 70-110 degrees C preferably, and overall reaction time amount is about 1 - 15 hours. As for this reaction, it is desirable to carry out under anhydrous conditions substantially in order to prevent the polycondensation reaction of the alkoxysilane partial condensate (3) itself. Moreover, manufacture of the resin (A) concerned can also be performed under reduced pressure of 10 - 30kPa extent. By the way, the alkoxy group content silane modified epoxy resin (A) manufactured under a non-solvent has the advantage which can be used as it is as ingredients, such as the application used with a non-solvent, for example, adhesives, a fabrication article, and a sealing agent. In addition, it is going to apply to the non-solvent application concerned, and desolventization of the organic solvent solution of the alkoxy group content silane modified epoxy resin (A) manufactured under solvent existence may be decompressed and carried out. However, in the case of an anticipated-use solvent, since it is necessary to carry out desolventization to the bottom of a heating condition which exceeds 130 degrees C and the sol-gel reaction of an alkoxy group content silane modified epoxy resin (A) advances superfluously in this case, it is hard to acquire the alkoxy group content silane modified epoxy resin (A) made into the purpose.

[0033] Moreover, on the occasion of the above-mentioned dealcoholization condensation reaction, what does not carry out ring breakage of the epoxy ring among well-known catalysts conventionally for promotion of a reaction can be used. As this catalyst, a lithium, sodium, a potassium, a rubidium, caesium, magnesium, calcium, barium, strontium, zinc, aluminum, titanium, cobalt, germanium, tin, lead, antimony, arsenic, a cerium, boron, cadmium, an oxide of metal; these metals like manganese, an organic-acid salt, a halogenide, an alkoxide, etc. are raised, for example. Also in these, organic tin and organic-acid tin are especially desirable, and, specifically, a dibutyl tin JIRAU rate, tin octylate, etc. are effective.

[0034] In this way, in the obtained alkoxy group content silane modified epoxy resin (A), as long as an epoxy resin (1), an epoxy resin (2), and an alkoxysilane partial condensate (3) are amounts a little, while it has been unreacted, you may contain. In addition, an unreacted alkoxysilane partial condensate (3) serves as a silica according to hydrolysis and a polycondensation at the time of hardening with an epoxy resin hardened material (B), and is combined with an alkoxy group content silane modified epoxy resin (A). The alkoxy group content silane modified epoxy resin (A) in this invention has the alkoxy group originating in an alkoxysilane partial condensate (3) in the molecule. Although especially limitation is not carried out for the content of the alkoxy group concerned, this alkoxy group by heat-treatment or the reaction with moisture (moisture) Since it is needed in order to form a sol-gel reaction and the hybrid hardened material which carried out dealcoholization condensation and which was combined mutually, An alkoxy group content silane modified epoxy resin (A) is usually good % and to 95-mol hold [40 of the alkoxy group of the alkoxysilane partial condensate (3) used as a reaction raw material -] 50 - 90-mol % preferably, while it has been unreacted it. [it] [it] This hybrid hardened material has the gelled detailed silica part (high order network structure of siloxane association).

[0035] In this invention, it is used as a silane modified epoxy resin constituent which comes to combine the curing agent for epoxy resins (B) with an alkoxy group content silane modified epoxy resin (A). If it hits applying the silane modified epoxy resin constituent of this invention to various applications, various kinds of epoxy resins can also be used together according to an application. Said bisphenol mold epoxy resin indicated as a constituent of this invention as the epoxy resin concerned which can be used together (1), Novolak mold epoxy resins, such as polyglycidyl ether of o-cresol-form aldeyde novolac and a phenol novolak mold epoxy resin; A phthalic acid, The glycidyl ester mold epoxy resin which polybasic acid and epichlorohydrin, such as dimer acid, are made to react, and is obtained; Diamino diphenylmethane, the line oxidized and obtained by peroxy acids, such as a peracetic acid, in glycidyl amine mold epoxy resin; olefin association which polyamine and epichlorohydrin, such as isocyanuric acid, are made to react and is obtained — an aliphatic series epoxy resin, cycloaliphatic epoxy resin, etc. are raised.

[0036] Moreover, as a curing agent for epoxy resins (B), the phenol resin system curing agent currently used as a curing agent of an epoxy resin, a polyamine system curing agent, a polycarboxylic acid system curing agent, an imidazole system curing agent, etc. can usually be especially used without a limit. Specifically as a thing of a phenol

resin system Phenol novolak resin, bisphenol novolak resin, a Pori p-vinyl phenol, etc. are raised. As a polyamine system curing agent, diethylenetriamine, triethylenetetramine, Tetraethylenepentamine, a dicyandiamide, a polyamide amine (polyamide resin), A ketimine compound, isophorone diamine, meta xylene diamine, m-phenylenediamine, 1, 3-screw (aminomethyl) cyclohexane, N-aminoethyl piperazine, The 4 and 4'-diamino diphenylmethane, 4, and 4'-diamino -3, 3'-diethyl diphenylmethane, Diamino diphenyl sulfone, a dicyandiamide, etc. are raised. As a polycarboxylic acid system curing agent Phthalic anhydride, tetrahydro phthalic anhydride, methyl cyclohexene-dicarboxylic anhydride, 3 and 6- and methylene tetrahydro phthalic anhydride, hexa KURORUENDO methylene tetrahydro phthalic anhydride, Methyl -3, 6-, and methylene tetrahydro phthalic anhydride are raised. As an imidazole system curing agent A KISHIRU imidazole, 2-undecylimidazole, 2-phenyl imidazole, 1-cyano ethyl-2-phenyl imidazolium trimellitate, 2-phenyl imidazolium isocyanurate, etc. are raised to 2-methylimidazole and 2-ethyl. It reacts with an epoxy ring and the above-mentioned curing agent for epoxy resins (B) not only carries out ring breakage hardening, but serves as a catalyst of the reaction in which the alkoxy silyl part and alkoxy group in an alkoxy group content silane modified epoxy resin (A) carry out siloxane condensation mutually. Also in the above-mentioned curing agent for epoxy resins (B), the polyamine system curing agent fits most the curing catalyst of an alkoxy silyl part or an alkoxy group, and is the optimal as a curing agent (B) of an alkoxy group content silane modified epoxy resin (A).

[0037] The operating rate of the curing agent for epoxy resins (B) is blended and prepared at a rate from which the functional group which has active hydrogen in a curing agent usually becomes about 0.2-1.5Eq to 1Eq of epoxy groups in an alkoxy group content silane modified epoxy resin constituent.

[0038] Moreover, in said epoxy resin constituent, the hardening accelerator for promoting the hardening reaction of an epoxy resin and a curing agent can be contained. For example, 1 and 8-diazabicyclo [5.4.0] undecene -7, triethylenediamine, Benzyl dimethylamine, triethanolamine, dimethylamino ethanol, The third class amines, such as a tris (dimethyl aminomethyl) phenol; 2-methylimidazole, 2-phenylimidazole, 2-phenyl-4-methylimidazole, Imidazole derivatives, such as 2-heptadecylimidazole; Tributyl phosphine, Methyl diphenylphosphine, triphenyl phosphine, diphenylphosphine, Organic phosphines, such as a phenyl phosphine; Tetra-phenyl phosphonium tetraphenyl borate, Tetraphenylboron salts, such as 2-ethyl-4-methylimidazole tetraphenyl borate and N-methyl morpholine tetraphenyl borate, etc. can be raised. As for a hardening accelerator, it is desirable to use it at a rate of 0.1 - 5 weight section to the 100 weight sections of an epoxy resin.

[0039] An organic solvent, a bulking agent, a release agent, a finishing agent, a flame retarder, a viscosity modifier, a plasticizer, an antimicrobial agent, an antifungal agent, a leveling agent, a defoaming agent, a coloring agent, a stabilizer, a coupling agent, etc. may be blended with said epoxy resin constituent in the range which does not spoil the effectiveness of this invention if needed.

[0040] In using the aforementioned silane modified epoxy resin constituent as various coating agents, adhesives, and a sealing agent, to the solid residue 100 weight section of a silane modified epoxy resin constituent, conventionally, 0-150 weight section combination is carried out, and it uses a well-known pigment. When using said resin constituent outdoors, it is desirable to blend sol-gel curing catalysts, such as a well-known acid or a well-known basic catalyst, and a metal system catalyst, conventionally. The amount of said catalyst used can be suitably decided with the activity of the catalyst to be used. usually, the alkoxy group of the alkoxy group content silane modified epoxy resin (A) to be used — receiving — the mole fraction — high Para toluenesulfonic acid, tin octylate, etc. of catalytic activity — about 0.01-5 mol %, the low formic acid of catalytic activity, an acetic acid, etc. — about 0.1-50 mol % — it is used. Furthermore, an epoxy resin, alkyd resin, and a mallein-ized oil may be blended for the hardening film for flexible-izing and the purpose which toughens.

[0041] In order to obtain a hybrid hardened material from a silane modified epoxy resin constituent directly, the above-mentioned epoxy resin constituent is stiffened at room temperature -250 degree C. Curing temperature is suitably determined by the curing agent for epoxy resins (B). As the curing agent (B) concerned, when using a phenol resin system curing agent and a polycarboxylic acid system curing agent, it is desirable to use a sol-gel curing catalyst together 0.1% or more in addition to the curing agent (B) concerned, and to make it harden at 150-250 degrees C. Although room temperature -100 degree C cold cure is possible if a polyamine system curing agent is used, it is desirable to use together sol-gel curing catalysts with high activity, such as tin octylate, 0.3% or more, and to stiffen them. Because, at the sol-gel hardening reaction of an alkoxy silyl part, when the alcohol concerned is generated after hardening by the ring breakage and crosslinking reaction of the epoxy group in an alkoxy group content silane modified epoxy resin (A) and an epoxy group with the curing agent for epoxy resins (B) advanced since alcohol is generated, foaming and a crack are produced. Therefore, it is necessary to adjust a sol-gel hardening reaction rate by choosing a catalyst suitably.

[0042] In order to obtain a semi-hardening film and the middle ingredient for shaping from a silane modified epoxy resin constituent, it is desirable to blend the sol-gel curing catalyst of a tin system, using latency curing agents, such as a phenol resin system curing agent, a polycarboxylic acid system curing agent, imidazole derivatives, and ketimines, as an epoxy curing agent (B) of the above-mentioned epoxy resin constituent. In order to produce a semi-hardening film and the middle ingredient for shaping using an epoxy resin constituent, it is necessary by heating below 40-150 degrees C preferably to advance a sol-gel hardening reaction so that siloxane association by sol-gel hardening may be made to generate 90% or more preferably 70% or more in an epoxy resin constituent. Because, since alcohol is generated at the sol-gel hardening reaction of an alkoxy silyl part, when there is little advance of sol-gel hardening at the time of semi-hardening object production, it is because hardening contraction, and a crack and foaming may arise in the full hardening reaction which follows this.

[0043] Furthermore, after thermoforming or thermocompression bonding, full hardening of such a semi-hardening object is usually carried out at 160-degree-C or more temperature of 250 degrees C or less, and it is led to an epoxy resin-silica hybrid hardened material.
[0044]
[Effect of the Invention] The epoxy resin constituent of this invention can be used for extensive applications, such as coating agents, such as a coating, adhesives, and a sealing agent, and is especially useful as an insulating coating agent, the charge of a printed-circuit radical plate, IC sealing agent, an insulating sealing compound, etc. The semi-hardening object (sol-gel hardened material) obtained from the epoxy resin constituent of this invention is flexible, and since it is rich in fabrication nature, it is useful as middle ingredients, such as a shaping middle ingredient, prepreg, and encapsulant. Moreover, the hardened material (perfect hardened material) obtained from the epoxy resin constituent of this invention does not have a crack etc., is transparent, and is a high degree of hardness. It excels in adhesion, electric insulation, etc. and, moreover, excels in thermal resistance (it does not soften at an elevated temperature, but an expansion coefficient is small, and it is heat-resistant adhesion). Therefore, it is useful as molding materials, such as the aforementioned extensive application especially the electrical and electric equipment and electronic parts, components for automobiles, an engineering-works building material, and a sporting gear ingredient.
[0045]
[Example] Hereafter, the example of manufacture, the example of comparison manufacture, an example, and the example of a comparison are given, and this invention is explained concretely. In addition, among each example, % is weight criteria, as long as he has no special mention.
[0046] The example 1 (manufacture of an alkoxy group content silane modified epoxy resin (A)) of manufacture 300g (the Tohto Kasei Co., Ltd. make, a trade name "EPO TOTO YD-011", weight-per-epoxy-equivalent 475 g/eq, m= 2.2) of the bisphenol A mold epoxy resins and 1250g (the Tohto Kasei Co., Ltd. make, a trade name "EPO TOTO YD-127", weight-per-epoxy-equivalent 190 g/eq, m= 0.11) of the bisphenol A mold epoxy resins were added to the agitator, the Bunsui machine, the thermometer, and the reactor equipped with nitrogen entrainment opening, and it was made to dissolve in them at 80 degrees C. Furthermore, 2.0g of dibutyltin laurate was added as Pori (methyl trimetoxysilane) (product [made from Tama Chemistry], trade name "MTMS-A", average repeat number of unit 3.5) 581.2g, and a catalyst, and the demethanol reaction was carried out at 100 degrees C under the nitrogen air current for 8 hours. The alkoxy group content silane modified epoxy resin (henceforth resin (A-1)) was obtained after cooling at 60 more degrees C by removing completely the methanol decompressed and dissolved in 13kPa. In addition, weight of the weight/epoxy resin (2) of the epoxy resin at the time of preparation (1) = it is weight-per-epoxy-equivalent =245 g/eq of 0.24 and bisphenol mold epoxy resin mixture ((1) + (2)). Moreover, weight of the silica equivalent weight / bisphenol mold epoxy resin mixture of an alkoxysilane partial condensate (3) (operating weight ratio) = it was 0.20. By 1 H-NMR (CDCl3 solution) measurement of resin (A-1), it has checked that the methine peak (near 3.3 ppm) of an epoxy ring is held 100%, and that the peak (near 3.85 ppm) of the hydroxyl group in an epoxy resin had disappeared. The weight per epoxy equivalent of resin (A-1) was 280 g/eq.
[0047] 193.3g (trade name "EPO TOTO YD-011") of the bisphenol A mold epoxy resins and the 1104.8 g bisphenol A mold epoxy resin (trade name "EPO TOTO YD-134") were added to the same reactor as the example 1 of example of manufacture 2 manufacture, and it was made to dissolve in it at 80 degrees C. Furthermore, 2.0g of dibutyltin laurate was added as Pori (methyl trimetoxysilane) (trade name "MTMS-A") 374.5g and a catalyst, and the demethanol reaction was carried out at 100 degrees C under the nitrogen air current for 8 hours. The alkoxy group content silane modified epoxy resin (henceforth resin (A-2)) was obtained after cooling at 60 more degrees C by removing completely the methanol decompressed and dissolved in 13kPa. In addition, weight of the weight/epoxy resin (2) of the epoxy resin at the time of preparation (1) = it is weight-per-epoxy-equivalent =283 g/eq of 0.17 and bisphenol mold epoxy resin mixture. Moreover, weight of the silica equivalent weight / bisphenol mold epoxy resin mixture of an alkoxysilane partial condensate (3) = it was 0.16. By 1 H-NMR (CDCl3 solution) measurement of resin (A-2), it has checked that the methine peak of an epoxy ring is held 100%, and that the peak of the hydroxyl group in an epoxy resin had disappeared. The weight per epoxy equivalent of resin (A-2) was 340 g/eq.
[0048] 350.0g (trade name "EPO TOTO YD-011") of the bisphenol A mold epoxy resins and 1050g (trade name "EPO TOTO YD-127") of the bisphenol A mold epoxy resins were added to the same reactor as the example 1 of example of manufacture 3 manufacture, and it was made to dissolve in it at 80 degrees C. Furthermore, 2.0g of dibutyltin laurate was added as Pori (methyl trimetoxysilane) (trade name "MTMS-A") 678g and a catalyst, and the demethanol reaction was carried out at 100 degrees C under the nitrogen air current for 8 hours. The alkoxy group content silane modified epoxy resin (henceforth resin (A-3)) was obtained after cooling at 60 more degrees C by removing completely the methanol decompressed and dissolved in 13kPa. In addition, weight of the weight/epoxy resin (2) of the epoxy resin at the time of preparation (1) = it is weight-per-epoxy-equivalent =261 g/eq of 0.33 and epoxy resin mixture. Moreover, weight of the silica equivalent weight / bisphenol mold epoxy resin mixture of an alkoxysilane partial condensate (3) = it was 0.25. By 1 H-NMR (CDCl3 solution) measurement of resin (A-3), it has checked that the methine peak of an epoxy ring is held 100%, and that the peak of the hydroxyl group in an epoxy resin had disappeared. The weight per epoxy equivalent of resin (A-3) was 320 g/eq.
[0049] The example of comparison manufacture 1 bisphenol A mold epoxy resin (trade name "EPO TOTO YD-127") was used as it was. Hereafter, this resin is called resin (a-1).
[0050] 300g (trade name "EPO TOTO YD-011") of the bisphenol A mold epoxy resins and 1250g (trade name "EPO TOTO YD-127") of the bisphenol A mold epoxy resins were added to the same reactor as the example 1 of example

of comparison manufacture 2 manufacture, and it was made to dissolve in it at 80 degrees C. The epoxy resin constituent was obtained by mixing Pori (methyl trimetoxysilane) (trade name "MTMS-A") 581.2g further after cooling to a room temperature. Hereafter, this resin constituent is called resin (a-2). Weight =0.24 of the weight/epoxy resin (2) of the epoxy resin at the time of preparation (1), weight per epoxy equivalent of bisphenol mold epoxy resin mixture = it is 245g/eq. Moreover, weight of the silica equivalent weight / bisphenol mold epoxy resin mixture of an alkoxysilane partial condensate (3) = it is 0.20. The weight per epoxy equivalent of resin (a-2) was 280 g/eq.

[0051] 1550g (trade name "EPO TOTO YD-127") of the bisphenol A mold epoxy resins was added to the same reactor as the example 1 of example of comparison manufacture 3 manufacture, and it was made to dissolve in it at 80 degrees C. Furthermore, 2.0g of dibutyltin laurate was added as Pori (methyl trimetoxysilane) (trade name "MTMS-A") 581.2g and a catalyst, and the demethanol reaction was carried out at 100 degrees C under the nitrogen air current for 8 hours. The alkoxy group content silane modified epoxy resin (henceforth resin (a-3)) was obtained after cooling at 60 more degrees C by removing completely the methanol decompressed and dissolved in 13kPa. In addition, weight of the weight/epoxy resin (2) of the epoxy resin at the time of preparation (1) = it was weight-per-epoxy-equivalent =190 g/eq of 0 and epoxy resin mixture. Moreover, weight of the silica equivalent weight / bisphenol mold epoxy resin mixture of an alkoxysilane partial condensate (3) = it was 0.20. By 1 H-NMR (CDCl3 solution) measurement of resin (a-3), it has checked that the methine peak of an epoxy ring is held 100%, and that the peak of the hydroxyl group in an epoxy resin had disappeared. The weight per epoxy equivalent of resin (a-3) was 260 g/eq.

[0052] 1250g (trade name "EPO TOTO YD-011") of the bisphenol A mold epoxy resins and 300g (trade name "EPO TOTO YD-127") of the bisphenol A mold epoxy resins were added to the same reactor as the example 1 of example of comparison manufacture 4 manufacture, and it dissolved in it at 80 degrees C. Furthermore, 2.0g of dibutyltin laurate was added as Pori (methyl trimetoxysilane) (trade name "MTMS-A") 581.2g and a catalyst, and under the nitrogen air current, when it was made to react at 100 degrees C for 1 hour, it gelled. In addition, it is the weight / epoxy resin (2) =4.2 of the epoxy resin at the time of preparation (1). Moreover, weight of the silica equivalent weight / bisphenol mold epoxy resin mixture of an alkoxysilane partial condensate (3) = it was 0.20.

[0053] In addition to each resin obtained in examples 1-3 and the example 1 of a comparison - the examples 1-3 of 3 manufactures, and the examples 1-3 of comparison manufacture, each epoxy resin constituent was prepared at a rate that weight per epoxy equivalent / amine equivalent becomes 1/1 about triethylenetetramine (equivalent of 24g / eq).

[0054] The container (vertical x horizontal x depth =10cmx10cmx1.5cm) by which fluororesin coating was carried out so that it might become about 300 micrometers of thickness was filled with each epoxy resin constituent obtained in examples 1-3 and the examples 1-3 of a comparison, and hardening was performed at 120 degrees C for 1 hour. The following criteria estimated the condition (contraction, appearance) of the obtained hardening film. A result is shown in Table 1.

[0055] (Contraction)

O : there is no crack in a hardened material.

**: A crack exists in a hardened material.

x: Many cracks are in a hardened material.

[0056] (Appearance)

O : transparence.

**: There is cloudiness.

x: It has milked.

[0057]

[Table 1]

	シラン変性エポキシ樹脂の種類	硬化物の評価結果	
		収縮	外観
実施例1	A－1	○	○
実施例2	A－2	○	○
実施例3	A－3	○	○
比較例1	a－1	○	○
比較例2	a－2	△	×
比較例3	a－3	○	△

[0058] In each example and the example 1 of a comparison, the transparent hardening film was obtained by each so that clearly from Table 1. However, the hardening film obtained in the example 2 of a comparison was milked by the phase separation of an epoxy resin and a silica, and was moreover very weak.

[0059] (Thermal resistance) The hardening film obtained in examples 1 and 2 and the examples 1 and 3 of a comparison was cut into 6mmx25mm, the dynamic storage modulus was measured using the viscoelasticity measuring instrument (rheology company make, a trade name "DVE-V4", a Measuring condition: a part for the amplitude of 1 micrometer, the vibration frequency of 10Hz, and slope 3 degree-C/), and thermal resistance was evaluated. A measurement result is shown in drawing 1 .

[0060] Compared with the example 1 of a comparison, the glass transition point of a hardening film is going up, and its elastic modulus in an elevated temperature is also high, and it is excellent in thermal resistance with examples 1 and 2 and the example 3 of a comparison so that clearly from drawing 1.
[0061] (Linear-expansion nature) The coefficient of linear expansion of 40-100 degrees C was measured using the hardening film obtained in examples 1 and 2 and the example 1 of a comparison with thermal stress distortion-measurement equipment (the product made from SEIKO Electronic industry, trade name TMA120C).
[0062]
[Table 2]

	線膨張率 (ppm)
実施例１	５８
実施例２	５５
比較例１	７４

[0063] (Electrical property) A dielectric constant and dielectric loss were measured on the frequency of 1MHz using the hardening film obtained in examples 1 and 2 and the example 1 of a comparison. A result is shown in Table 3.
[0064]
[Table 3]

	誘電率	誘電損失
実施例１	３．７	０．０１６
実施例２	３．６	０．０１６
比較例１	４．２	０．０１５

[0065] It was admitted that examples 1 and 2 are excellent in insulation as contrasted with the example 1 of a comparison and that there was no difference in dielectric loss.
[0066] In addition, each epoxy resin constituent was prepared at a rate that weight per epoxy equivalent / amine equivalent becomes 1/1 about amino polyamide resin (the Tohto Kasei Co., Ltd. make, a trade name "good MAIDO G-725", equivalent 130 g/eq), to each resin obtained in examples 4 and 5 and the example 4 of a comparison, the examples 1 and 2 of 5 manufactures, and the examples 1 and 3 of comparison manufacture. The adhesion of these constituents and heat-resistant adhesion were measured on condition that the following, and the property as a charge of a binder was mainly evaluated.
[0067] (Adhesion) JIS after having applied each resin constituent so that it might become a glass plate, mortar, and an aluminum plate with 20 micrometers of thickness, and stiffening it at 130 degrees C for 30 minutes The grid cellophane tape friction test by General Test Procedures of K-5400 was performed, and it judged on the following criteria. An evaluation result is shown in Table 4.
O --- [--- 69 - 0/100 [0068]] 100/100O --- 99-95/100** --- 94-70/100x
[Table 4]

	シラン変性エポキシ樹脂の種類	ガラス板	モルタル	アルミ板
実施例４	Ａ－１	◎	○	◎
実施例５	Ａ－２	◎	○	◎
比較例４	ａ－１	○	△	△
比較例５	ａ－３	◎	△	◎

[0069] (Heat-resistant adhesion) After leaving the trial version used for the adhesion test at 180 degrees C for 8 hours, the grid cellophane tape friction test was performed and it judged with the above on the same criteria. A result is shown in Table 5.
[0070]
[Table 5]

	ガラス板	モルタル	アルミ板
実施例４	◎	○	◎
実施例５	◎	○	◎
比較例４	○	×	△
比較例５	◎	△	◎

[0071] To each resin obtained in examples 6-8 and the example 6 of a comparison - the examples 1-3 of 8 manufactures, and the examples 1-3 of comparison manufacture, in addition, amino polyamide resin (trade name "good MAIDO G-725") was diluted with the rate that weight per epoxy equivalent / amine equivalent becomes 1/1, to 50% by methyl isobutyl ketone, and each epoxy resin constituent was prepared.
[0072] (**********-proof) JIS after having applied each resin constituent so that it might become an aluminum plate with 20 micrometers of thickness, and stiffening it at 130 degrees C for 30 minutes The pencil scratch test by the coating commercial-test approach of K-5400 was performed. A result is shown in Table 6.
[0073]
[Table 6]

	シラン変性エポキシ樹脂の種類	アルミ板
実施例6	A－1	3H
実施例7	A－2	4H
実施例8	A－3	4H
比較例6	a－1	2H
比較例7	a－2	3H
比較例8	a－3	2H

[0074] After, stirring the solution which diluted novolak mold phenol resin (the product made from Arakawa Chemical industry, trade name TAMANORU 759) with the methyl ethyl ketone to 50% at a room temperature in addition for 30 minutes with a rate that weight per epoxy equivalent / phenol equivalent becomes 1/1, to the resin (A-1) obtained in the example 1 of example 9 manufacture, tin octylate was added 1% per solid content, and it considered as the epoxy resin constituent. The container (vertical x horizontal x depth =10cmx10cmx1.5cm) by which fluororesin coating was carried out was filled with this epoxy resin constituent, by leaving it at 30 minutes and 130 degrees C in 80 degrees C for 30 minutes, sol-gel hardening was carried out and the semi-hardening sheet of the shape of rubber of 300 micrometers of thickness was obtained. The obtained semi-hardening sheet is flexible (the maximum elongation percentage is about 15%), and was able to carry out fabrication above 50 degrees C. The semi-hardening object obtained like the above was heated at 100 degrees C, and metal mold (10mmx60mmx2mm) was filled up. Press forming was carried out by 200 degrees C and 1x107Pa, and the epoxy resin-silica hybrid moldings was obtained. This epoxy resin-silica hybrid showed the same thermal resistance as the hardened material of an example 1.
[0075] After, stirring the dimethylformamide solution (10% of concentration) of a dicyandiamide at a room temperature in addition for 30 minutes with a rate that weight per epoxy equivalent / amine equivalent becomes 1/1, to the resin (A-1) obtained in the example 1 of example 10 manufacture, tin octylate was added 1% per solid content, and it considered as the epoxy resin constituent. The container (vertical x horizontal x depth =10cmx10cmx1.5cm) by which fluororesin coating was carried out was filled with this epoxy resin constituent, sol-gel hardening was carried out by leaving it at 30 minutes and 110 degrees C in 80 degrees C for 30 minutes, and the semi-hardening sheet without the surface tuck of 100 micrometers of thickness was obtained. The maximum elongation percentage of the obtained semi-hardening sheet was about 8%. It inserted with two aluminum plates, heating this semi-hardening sheet at 120 degrees C, and was stuck by pressure by 1x107Pa. Subsequently, full hardening of this was carried out at 210 degrees C, and the epoxy resin-silica hybrid was obtained.
[0076] After, stirring the novolak mold phenol resin (trade name TAMANORU 759) fused at 130 degrees C at 80 degrees C in addition for 30 minutes with a rate that weight per epoxy equivalent / phenol equivalent becomes 1/1, to the resin (a-3) obtained in the example of example of comparison 9 comparison manufacture, tin octylate was added 1% per solid content, and it considered as the epoxy resin constituent. The container (vertical x horizontal x depth =10cmx10cmx1.5cm) by which fluororesin coating was carried out was filled with this epoxy resin constituent, hardening was performed at 100 degrees C for 30 minutes, and the semi-hardening sheet of 300 micrometers of thickness was obtained. The obtained semi-hardening sheet had a surface tuck, and since it was weak, it was not able to measure elongation percentage.

[Translation done.]